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(71) Applicant (*for all designated States except US*): **ALBEMARLE CORPORATION** [US/US]; 451 Florida Street, Baton Rouge, LA 70801-1765 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **SANGOKOYA, Samuel, A.** [US/US]; 10665 Lynell Street, Baton Rouge, LA 70815 (US). **GOODALL, Brian, L.** [GB/US]; 1259 Appalachian Road, Ambler, PA 19002 (US).

(74) Agents: **PIPPENGER, Philip, M.** et al.; Albemarle Corporation, Law Department, 451 Florida Street, Baton Rouge, LA 70801-1765 (US).

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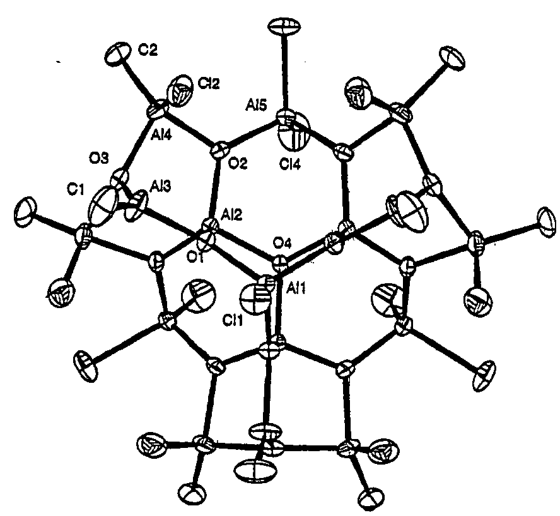
(54) Title: HYDROCARBYLHALOALUMINO XANES

Chloro-Methylaluminoxane
(C-MAO)

$Me_9Al_{16}O_{13}Cl_{13}$



(57) Abstract: Discrete hydrocarbylhaloaluminoxane compounds having a molecular weight of above 1000 and defined ratio of hydrocarbyl groups, aluminum atoms, and oxygen atoms in the molecule are provided. These compounds can have an X-ray crystal structure and/or a cluster of fused hexagonal rings consisting of A1 and O atoms having the formula $[(XA1O)_6O]$ and having the general formula $R_9A1_{16}O_{13}X_{13}$ where R is a hydrocarbyl group (e.g., Me or Et) and X is a halogen atom (e.g., F or C1). They can be interacted with known inorganic or organometallic olefin polymerization catalyst compounds to form active polymerization catalysts. Such catalysts of the hydrocarbylhaloaluminoxane compounds can be supported on organic or inorganic catalyst supports or carriers, and the supported or unsupported catalysts can be used to polymerize polymerizable olefins such as ethylene and/or propylene with or without higher α-olefins.

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HYDROCARBYLHALOALUMINOXANES

[0001] The work leading to the invention described in this patent application was performed pursuant to a contract with an agency of the United States Government. The contract is Cooperative Agreement No. 70NANBOH3049 between Albemarle Corporation and the National Institute of Standards and Technology of the United States Department of Commerce (Advanced Technology Program).

TECHNICAL FIELD

[0002] This invention relates to new organoaluminum compositions which are especially useful as discrete and stoichiometric activators in the preparation of new highly efficacious catalyst compositions.

BACKGROUND

[0003] Hydrocarbylaluminoxane compositions are generally obtained by hydrolyzing hydrocarbylaluminum compounds such as alkyl aluminum compounds with water e.g., by direct water addition, contact with a water-wet material such as a solvent containing water or a solid substrate such as a porous catalyst support wet with or soaked in water, or via salt hydrate addition. The resulting products depending on the amount of added water are dimeric or complex mixtures of oligomeric aluminoxanes. Hitherto a discrete organohaloaluminoxane compound having a molecular weight of above 1000 and a defined ratio of hydrocarbyl groups, aluminum atoms, oxygen atoms, and halogen atoms has not been identified. Nor has a discrete organohaloaluminoxane compound characterizable by an X-ray crystal structure ever been isolated.

[0004] To date, the most commonly used aluminoxane is methylaluminoxane (MAO). MAO is relatively expensive due to the high cost of the raw material, trimethylaluminum (TMA). There is therefore a need for a low cost aluminoxane activator in order to reduce the total catalyst cost.

[0005] Recent disclosures in WO 00/22007 published, April 20, 2000 and U.S. Pat. No. 6,306,986, granted October 23, 2001, describe the use as catalyst activators of haloaluminoxanes which are ill-defined dimeric/oligomeric mixtures and which are acknowledged in these disclosures to be composed of many individual species which may be in dynamic equilibria.

SUMMARY OF THE INVENTION

[0006] This invention fulfills the above need, and at the same time utilizes low cost raw materials that result in the provision of discrete compounds characterizable by X-ray crystal structure.

[0007] In accordance with one embodiment of this invention there is provided a discrete

hydrocarbylhaloaluminoxane compound having a molecular weight of above 1000 and a defined ratio of hydrocarbyl groups, aluminum atoms, and oxygen atoms in the molecule. In a preferred embodiment such compound is characterized by having an X-ray crystal structure.

[0008] In a preferred embodiment of this invention the hydrocarbylhaloaluminoxane is a discrete hydrocarbylhaloaluminoxane compound having a molecular weight of above 1000 and having in its core structure a cluster of fused hexagonal rings consisting of Al and O atoms, having the formula $[(XAlO)_6O)]$ and a peripheral structure with the formula $[R_3Al_3X_2O]$ where R is a hydrocarbyl group, preferably an alkyl group, and more preferably a methyl or ethyl group, and X is a halogen atom, most preferably a chlorine atom. Still more preferably such compound is characterized by having an X-ray crystal structure.

[0009] Another preferred embodiment of this invention is a discrete hydrocarbylhaloaluminoxane compound having the formula:

$$R_9Al_{16}O_{13}X_{13}$$

where R is a hydrocarbyl group and X is a halogen atom.

[0010] In each of the above embodiments the halogen atoms are preferably fluorine or chlorine atoms, and more preferably are chlorine atoms.

[0011] In each of the above embodiments of this invention the hydrocarbyl groups in the hydrocarbylhaloaluminoxane preferably are saturated aliphatic, saturated cycloaliphatic, or aromatic hydrocarbyl groups, more preferably are alkyl groups, still more preferably are alkyl groups each having up to about 20 carbon atoms and more desirably up to about 10 carbon atoms, and even more preferably are primary alkyl groups each having up to about 4 carbon atoms, and most preferably are methyl or ethyl groups.

[0012] In each of the above embodiments the hydrocarbylhaloaluminoxane is most preferably supported on a catalyst support or carrier, preferably an inorganic catalyst support such as clay, more preferably on an inorganic catalyst support comprised of a zeolite or at least one oxide of a metal or metalloid element or mixtures thereof, still more preferably on silica, alumina, or silica-alumina, and most preferably on silica.

[0013] Methods for producing such supported hydrocarbylhaloaluminoxane compositions form further embodiments of this invention.

[0014] Another embodiment of this invention is a catalyst composition which comprises a product obtained by contacting (i) a metal compound or complex of a transition metal of Groups 3 to 11 of the Periodic Table, including the lanthanide series and the actinide series, and (ii) a hydrocarbylhaloaluminoxane of this invention, preferably on a catalyst support or carrier.

[0015] This invention also involves, *inter alia,* as especially preferred embodiments thereof, a catalyst composition comprised of a reaction product of a halide or pseudohalide (alkoxide, or oxyhalide), or other Ziegler-Natta transition metal catalyst compound and a

hydrocarbylhaloaluminoxane of this invention, preferably on a catalyst support or carrier. Such catalyst compositions of this invention, especially when on a catalyst support, enable the preparation of polyolefins such as polyethylene, polypropylene, and copolymers of either or both of these with other 1-olefin monomers.

[0016] Methods for producing such catalyst compositions and methods of polymerizing or copolymerizing olefinic monomers using such catalyst compositions form still further embodiments of this invention.

[0017] Other embodiments of the invention will be apparent from the ensuing description.

BRIEF DESCRIPTION OF THE DRAWING

[0018] Fig. 1 is view of the X-ray crystallographic structure of a particularly preferred crystalline hydrocarbylhaloaluminoxane of this invention.

FURTHER DETAILED DESCRIPTION OF THIS INVENTION

[0019] This invention makes it possible for the first time ever to provide a discrete aluminoxane of well-defined composition and structure having a molecular weight above 1000. By "well-defined composition and structure" is meant that the aluminoxane is characterizable by procedures such as X-ray crystallography.

[0020] This invention also makes it possible to provide a catalyst of a halide, alkoxide or mixed halide-alkoxide of a Group 3 to 6 metal, and especially a Group 4 to 6 transition metal halide catalyst capable of producing polyethylene and ethylene copolymers. Such catalyst is preferably supported on a particulate catalyst support or carrier all as described hereinafter.

Hydrocarbylhaloaluminoxanes of this Invention

[0021] The hydrocarbylhaloaluminoxanes provided by this invention comprise discrete compounds having a definable chemical structure. These compounds have a molecular weight above 1000 and contain a plurality of aluminum atoms, a plurality of oxygen atoms, a plurality of halogen atoms, and a plurality of organic groups, typically hydrocarbyl groups such as alkyl groups or the like. In many cases, the compound will contain a cluster of alternating aluminum oxygen and aluminum atoms in a cyclic configuration.

[0022] An example of the novel hydrocarbylhaloaluminoxanes of this invention is an alkylhaloaluminoxane having a cluster of 16 aluminum atoms. A compound of this type has the general formula:

$$R_9Al_{16}O_{13}X_{13}$$

where R is a hydrocarbyl group. Illustrative hydrocarbyl groups include, for example, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, and cycloalkylalkyl. Typically these hydrocarbyl groups will contain no more than about 18 carbon atoms each, for example as linear or branched alkyl groups. More usually R is an alkyl group having up to about 10

carbon atoms, more preferably is a primary alkyl group having up to about 4 carbon atoms, and most preferably is methyl or ethyl. X in the above formula is a halogen atom (F, Cl, Br, I), preferably is a fluorine or chlorine atom, and most preferably is a chlorine atom. While it is possible for the hydrocarbyl groups and the halogen atoms to differ within the structure, preferably each hydrocarbyl group is the same and each halogen atom is the same in the composition. Mixtures of two or more compounds of the above formula are within the scope of this invention.

[0023] The unique structural characteristics of such compositions has enabled the synthesis, isolation and characterization of a polymerizationally-active crystalline hydrocarbylhaloaluminoxane of the formula:

$$[Me_3Al_3Cl_2O]_3[O_3AlCl][(ClAlO)_6O]$$

where Me is a methyl group. For convenience, this compound or composition is sometimes referred to hereinafter as C-MAO, which stands for crystalline MAO.

[0024] Another polymerizationally-active crystalline hydrocarbylhaloaluminoxane that has been synthesized, isolated and characterized has the formula:

$$[Et_3Al_3Cl_2O]_3[O_3AlCl][(ClAlO)_6O]$$

where Et is an ethyl group. For convenience, this compound or composition is sometimes referred to hereinafter as C-EAO, which stands for crystalline EAO.

[0025] Other non-limiting examples of hydrocarbylhaloaluminoxanes of this invention include $[Me_3Al_3F_2O]_3[O_3AlF][(FAlO)_6O]$ and $[Et_3Al_3F_2O]_3[O_3AlF][(FAlO)_6O]$.

[0026] The compositions of this invention can be prepared by controlled partial hydrolysis of a hydrocarbylaluminum halide, such as a dialkylaluminum halide. Of particular importance is use of a proper molar ratio of water to the particular hydrocarbylaluminum halide being used as the reactant in the process. Such molar ratio is relatively narrow and is deemed dependent upon the identity of the type and/or composition of the particular hydrocarbylaluminum halide being used in the reaction. In fact, the existence of crystallizable compositions of this invention only became known after several prior attempts had failed to produce a discrete, well-definable composition using attempted controlled hydrolysis of a dialkylaluminum halide. Thus, for example, the molar proportions for producing discrete haloaluminoxane compositions of this invention from a dihydrocarbylaluminum halide such as dimethylaluminum chloride or diethylaluminum chloride and lithium hydroxide monohydrate as the water source are about 0.8-1.0 mole of aluminum per mole of $LiOH \bullet H_2O$. Since the reaction is exothermic, temperatures are typically kept below about 80°C. Such controlled partial hydrolysis can thus be initiated at room temperature or at temperatures below room temperature, e.g., -30°C.

[0027] Controlled partial hydrolysis may also be effected by use of such water sources as free water, organic solvents wet with water, porous materials which have absorbed water, or

hydrated metal salts. When free water or materials containing significant amounts of free water are used, it is desirable to maintain the reaction mixture at temperatures of below about 10°C and preferably at about 0°C or below. On the other hand when hydrated metal salts are used, the reaction typically can be initiated at room temperature or even at temperatures below room temperature, and in any event the reaction mixture should be kept below about 80°C.

[0028] Because it is difficult to control the hydrolysis reaction when using water per se, even with vigorous agitation of the mixture, the controlled hydrolysis is preferably conducted by adding the free water in the form of a solution or a dispersion in an organic solvent to the hydrocarbylaluminum halide.

[0029] When using a hydrated metal salt as the source of water for the controlled hydrolysis, any of a variety of hydrated salts can be used. Suitable hydrates include salt hydrates such as, for example, $CuSO_4 \cdot 5H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $FeSO_4 \cdot 7H_2O$, $AlCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Na_3PO_4 \cdot 12H_2O$, $LiBr \cdot 2H_2O$, $LiCl \cdot 1H_2O$, $LiI \cdot 2H_2O$, $LiI \cdot 3H_2O$, $KF \cdot 2H_2O$, $NaBr \cdot 2H_2O$ and alkali metal or alkaline earth metal hydroxide hydrates such as, for example, $NaOH \cdot H_2O$, $NaOH \cdot 2H_2O$, $Ba(OH)_2 \cdot 8H_2O$, $KOH \cdot 2H_2O$, $CsOH \cdot 1H_2O$, $LiOH \cdot 1H_2O$. Mixtures of any of the above hydrates can be used. The mole ratios of free water or water in the hydrate or in porous materials such as alumina or silica to total hydrocarbylaluminum halides in the mixture can vary, such as for example from about 2:1 to about 1:4, but as noted above the mole ratio of water to aluminum used in any given situation is dependent upon the particular hydrocarbylaluminum halide being subjected to the controlled hydrolysis. In any case where, in order to obtain the desired discrete hydrocarbylhaloaluminoxane of this invention, the appropriate mole ratio has not already been ascertained, a few preliminary experiments should be carried out in order to identify the optimum mole ratio for achieving the formation of such discrete hydrocarbylhaloaluminoxane.

[0030] At present the preferred hydrolytic agent for use in preparing the hydrocarbylhaloaluminoxanes of this invention is an alkali metal hydroxide hydrate, most preferably lithium hydroxide monohydrate.

[0031] U.S. Patent Nos. 4,908,463; 4,924,018; 5,003,095; 5,041,583; 5,066,631; 5,099,050; 5,157,008; 5,157,137; 5,235,081; 5,248,801, and 5,371,260, whose entire teachings are incorporated herein by reference, describe processing techniques which can be utilized in conducting the controlled partial hydrolysis of hydrocarbylaluminum halides when forming the composition of this invention.

[0032] Hydrocarbylaluminum halides which may be controllably hydrolyzed, for example with $LiOH \cdot H_2O$, to produce the compositions of this invention are dihydrocarbylaluminum halides, R_2AlX; hydrocarbylaluminum dihalides, $RAlX_2$; and hydrocarbylaluminum sesquihalides, $R_3Al_2X_3$. Of these, controlled partial hydrolysis of dihydrocarbylaluminum

halides is preferred.

Supported Catalysts and Catalyst Supports or Carrier Materials

[0033] Preferably, the controlled partial hydrolysis is performed in the presence of a slurry or suspension of a particulate catalyst support or carrier material in an inert diluent. Suitable diluents include one or more paraffinic, cycloparaffinic or aromatic hydrocarbon diluents, or any mixture of any two or more of such diluents. In an alternative preferred method, the particulate catalyst support or carrier material is added to the controlled hydrolysis mixture during or after completion of the controlled partial hydrolysis but before any crystalline hydrocarbylhaloaluminoxane starts to form in the reaction mixture. In either such case, the hydrocarbylhaloaluminoxane is able to deposit on or otherwise interact with the support or carrier material. In the case of some support materials such as silica, the isolated supported hydrocarbylhaloaluminoxane can be converted apparently into another form of polymerization active supported product by maintaining the supported hydrocarbylhaloaluminoxane under a reduced pressure, and preferably while at a temperature in the range of about 25 to about 80°C. Pressures in the range of about 10 to about 60 mm Hg are usually sufficient to effect the apparent conversion in this temperature range. At least in some cases the apparent conversion of the supported hydrocarbylhaloaluminoxane from one form to another is evidenced by a visually perceivable color change in the product. The exact nature of what is taking place in the composition is not known. However it is known that both the initial supported hydrocarbylhaloaluminoxane and the resultant color-changed product on the support are very useful as cocatalysts in the practice of this invention.

[0034] Other methods can be used for forming the supported hydrocarbylhaloaluminoxane compositions of this invention. For example, the catalyst support can be treated in an inert organic diluent with a solution or slurry of a previously-isolated and inert solvent-washed discrete hydrocarbylhaloaluminoxane of this invention. Preferably such solution or slurry is maintained at a temperature in the range of about 10 to about 100°C, and preferably in the range of about 20 to about 60°C, with agitation.

[0035] Catalyst support materials used in the practice of this invention may be any finely divided inorganic solid support, such as talc, clay, silica, alumina, silica-alumina, or mixtures thereof or a particulate resinous support material such as spheroidal, particulate, or finely-divided polyethylene, polyvinylchloride, polystyrene, or the like. Preferred support materials are inorganic particulate solid catalyst supports or carrier materials such as magnesium halides, or the like, and particularly inorganic oxides, aluminum silicates, or inorganic compositions containing inorganic oxides, such as kaolinite, attapulgite, montmorillonite, illite, bentonite, halloysite, and similar refractory clays. Inorganic oxides that may be employed either alone or in combination with silica, alumina, or silica-alumina are magnesia, titania, zirconia. The inorganic oxides may be dehydrated to remove water. If desired, the

residual surface hydroxyl groups in the inorganic solid porous support may be removed by additional heating or by reaction with chemical dehydrating agents such as lithium alkyl, silylchloride, aluminum alkyls, or preferably with a hydrocarbylhaloaluminoxane. Preferred catalyst supports include dehydrated inorganic oxide treated with a hydrocarbylhaloaluminoxane, more preferably with an alkylhaloaluminoxane, still more preferably with an alkylchloroaluminoxane, such as methylchloroaluminoxane or ethylchloroaluminoxane. A suitable support material of this type is silica or silica gel treated with such hydrocarbylhaloaluminoxanes. When such a hydrocarbylhaloaluminoxane treated support is utilized in the production of the supported catalyst, it may not be necessary to include additional hydrocarbylhaloaluminoxane in the catalyst composition. Also preferred as a catalyst support is a wet gel, more preferably a wet silica gel, containing up to approximately 20% by weight absorbed water. Wet gels may be directly mixed with hydrocarbylaluminum halide in appropriate molar proportion to form the hydrocarbylhaloaluminoxane component of the catalyst system.

[0036] Particularly preferred as the support material is particulate silica, especially porous particulate silica.

[0037] The specific particle size, surface area and pore volume of the inorganic support material determine the amount of inorganic support material that is desirable to employ in preparing the catalyst compositions, as well as affecting the properties of polymers formed with the aid of the catalyst compositions. These properties are frequently taken into consideration in choosing an inorganic support material for use in a particular aspect of the invention. A suitable inorganic support such as silica typically will have a particle diameter in the range of 0.1 to 600 microns, preferably in the range of 0.3 to 100 microns; a surface area of in the range of 50 to 1000 m^2/g, preferably in the range of 100 to 500 m^2/g; and a pore volume of in the range of about 0.3 to 5.0 cc/g, preferably in the range of 0.5 to 3.5 cc/g. It is also desirable to employ supports with pore diameters of from about 50 to about 500 angstroms. To ensure its use in dehydrated form the support material may be heat treated at 100-1000°C for a period of 1-100 hours, preferably 3-24 hours. The treatment may be carried out in a vacuum or while purging with a dry inert gas such as nitrogen.

[0038] As an alternative, the support material may be chemically dehydrated. Chemical dehydration is accomplished by slurrying the support in an inert low boiling solvent such as, for example, heptane, in the presence of the dehydrating agent such as for example, triethylaluminum in a moisture and oxygen-free atmosphere.

Transition Metal Catalyst Compounds

[0039] The hydrocarbylhaloaluminoxanes of this invention are highly effective as cocatalysts, and can be used with any known transition metal catalyst compound in which the transition metal thereof is a Group 3 to 11 transition metal of the Periodic Table including

compounds of a metal of the lanthanide or actinide series, and which is known to be useful as a polymerization catalyst when used with an aluminum alkyl or aluminoxane. The Periodic Table referred to herein is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*. Suitable catalyst compounds can also be described as d- and f- block metal compounds. See, for example, the Periodic Table appearing on page 225 of Moeller, et al., *Chemistry*, Second Edition, Academic Press, copyright 1984. As regards the metal constituent, preferred are compounds of Cu, Fe, Co, Ni, Pd, and V. More preferred are compounds of the metals of Groups 4-6 (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W), and most preferred are the Group 4 metals, especially titanium, zirconium, or hafnium.

[0040] Thus the transition metal catalyst compounds used in this invention can be one or more of any Ziegler-Natta catalyst compound, any metallocene, any compound of constrained geometry, any late transition metal complex, or any other transition metal compound or complex reported in the literature or otherwise generally known in the art to be an effective catalyst compound when suitably activated, including mixtures of two or more different types of such transition metal compounds or complexes, such as for example a mixture of a metallocene and a Ziegler-Natta olefin polymerization catalyst compound.

[0041] Among the transition metal compounds of the metals of Groups 3, 4, 5, and 6 which can he used as the transition metal component of the catalyst compositions of and used in this invention are the compounds of such metals as scandium, titanium, zirconium, hafnium, cerium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, thorium and uranium often referred to as Ziegler-Natta type olefin polymerization catalysts. Preferred compounds of this type can be represented by the formula $MX_n(OR)_m$ in which M represents the transition metal atom or a transition metal atom cation containing one or two oxygen atoms such as vanadyl, zirconyl, or uranyl, X represents a halogen atom, OR represents a hydrocarbyloxy group having up to about 18 carbon atoms, preferably up to about 8 carbon atoms, and more preferably alkyl of up to about 4 carbon atoms, such as an alkyl, cycloalkyl, cycloalkylalkyl, aryl, or aralkyl, group and n and m are positive integers except that either one of them (but not both) can be zero, and where $n + m$ is the valence state of the transition metal. Illustrative of some of the transition metal compounds which can he used are, for example, titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride, titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium triiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, vanadium tetrabromide, vanadium tribromide, vanadium dibromide, vanadium

trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium diiodide, vanadium triiodide, vanadium tetraiodide, vanadyl chloride, vanadyl bromide, niobium pentabromide, niobium pentachloride, niobium pentafluoride, tantalum pentabromide, tantalum pentachloride, tantalum pentafluoride, chromous bromide, chromic bromide, chromous chloride, chromic chloride, chromous fluoride, chromic fluoride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide,molybdenum dichloride, molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, molybdenum hexafluoride, lanthanum trichloride, cerous fluoride, cerous chloride, cerous bromide, cerous iodide, ceric fluoride, uranium trichloride, uranium tetrachloride, uranium tribromide, uranium tetrabromide, thorium tetrachloride, thorium tetrabromide. Among the hydrocarbyloxides and mixed halide/hydrocarbyloxides of the transition metals are $Ti(OCH_3)_4$, $Ti(OCH_3)Cl_3$, $Ti(OCH_3)Br_3$, $Ti(OCH_3)_2I_2$, $Ti(OC_2H_5)_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, $Ti(OC_4H_9)Br_3$, $Ti(OC_2H_5)I_3$, $Ti(OC_3H_7)_2Cl_2$, $Ti(O\text{-iso-}C_3H_7)_3Cl$, $Ti(O\text{-iso-}C_3H_7)_2Cl_2$, $Ti(O\text{-iso-}C_3H_7)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_4H_9)_2Cl_2$, $Ti(OC_4H_9)Cl_3$, $Ti(OC_6H_5)Cl_3$, $Ti(O\text{-p-}CH_3C_6H_4)Cl_3$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_6H_{13})Cl_3$, $Ti(O\text{-cyclo-}C_6H_{11})Cl_3$, $Ti(OC_8H_{17})_2Br_2$, $Ti(O\text{-2-EtHex})_4$, $Ti(OC_{12}H_{25})Cl_3$, $Ti(OC_{17}H_{18})_2Br_2$, $Zr(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $Zr(OC_5H_{11})_4$, $ZrCl(OC_2H_5)_3$, $ZrCl_2(OC_2H_5)_2$, $ZrCl_3(OC_2H_5)$, $ZrCl(OC_4H_9)_3$, $ZrCl_2(OC_4H_9)_2$, $ZrCl_3(OC_4H_9)$, $Hf(OC_4H_9)_4$, $Hf(OC_4H_9)_3Cl$, $VO(OC_2H_5)_3$, $VOCl(OCH_3)_2$, $VOCl(OC_2H_5)_2$, $VOCl(OC_3H_7)_2$, $VOCl(O\text{-iso-}C_3H_7)_2$, $VOCl_2(OCH_3)$, $VOCl_2(OC_2H_5)$, $VOCl_2(OC_3H_7)$, $VOCl_2(O\text{-iso-}C_3H_7)$, $VOBr(OCH_3)_2$, $VOBr(OC_2H_5)_2$, $VOBr(O\text{-iso-}C_4H_9)_2$, $VOBr_2(OC_3H_7)$, $VOBr_2(O\text{-iso-}C_3H_7)$, $VOBr_2(OC_4H_9)$, $VOBr_2(O\text{-iso-}C_4H_9)$, $VOI(OCH_3)_2$, $VOI(OC_2H_5)_2$, $VOI_2(OCH_3)$, $VOI_2(O\text{-cyclo-}C_3H_5)$, $VOI_2(OC_5H_{11})$, $VOI_2(O\text{-cyclo-}C_6H_{11})$, $Cr(O\text{-iso-}C_4H_9)_3$, $Mo(OC_2H_5)_3$. Carboxylic acid salts and various chelates of the transition metal can also be used but in general are less preferred. A few non-limiting examples of such salts and chelates include zirconyl acetate, uranyl butyrate, chromium acetate, chromium(III) oxy-2-ethylhexanoate, chromium(III) 2-ethylhexanoate, chromium(III) dichloroethylhexanoate, chromium(II) 2-ethylhexanoate, titanium(IV) 2-ethylhexanoate, bis(2,4-pentanedionate)titanium oxide, bis(2,4-pentanedionate)titanium dichloride, bis(2,4-pentanedionate)titanium dibutoxide, vanadyl acetylacetonate, chromium acetylacetonate, niobium acetylacetonate, zirconyl acetylacetonate, chromium octylacetoacetate. Also, transition metal alkyls such as tetramethyl titanium, methyl titanium trichloride, tetraethyl zirconium, tetraphenyl titanium, can be used.

[0042] Preferred transition metal compounds of the well-known Ziegler-Natta catalyst compounds are those of the Group 4 metals, including the alkoxides, halides, and mixed halide/alkoxide compounds. More preferred are $TiCl_4$, $ZrCl_4$, $HfCl_4$, and $TiCl_3$, with $TiCl_4$ being most preferred. Such more preferred compounds can be used in chelated form in order to facilitate solubility. Suitable chelated catalysts of this type are known and reported in the literature.

[0043] Metallocenes are another broad class of olefin polymerization catalyst compounds with which the hydrocarbylhaloaluminoxanes of this invention can be used in forming novel highly effective catalysts of this invention. As used herein, the term "metallocene" includes metal derivatives which contain at least one cyclopentadienyl moiety. Suitable metallocenes are well known in the art and include the metallocenes of Groups 3, 4, 5, 6, lanthanide and actinide metals, for example, the metallocenes which are described in U.S. Pat. Nos. 2,864,843; 2,983,740; 4,665,046; 4,874,880; 4,892,851; 4,931,417; 4,952,713; 5,017,714; 5,026,798; 5,036,034; 5,064,802; 5,081,231; 5,145,819; 5,162,278; 5,245,019; 5,268,495; 5,276,208; 5,304,523; 5,324,800; 5,329,031; 5,329,033; 5,330,948, 5,347,025; 5,347,026; and 5,347,752, whose teachings with respect to such metallocenes are incorporated herein by reference.

[0044] Metallocene structures in this specification are to be interpreted broadly, and include structures containing at least one Cp or substituted Cp ring. Thus metallocenes suitable for use in this invention can be represented by Formula (I):

$$B_aCp_bMX_cY_d \qquad \text{(I)}$$

where Cp, independently in each occurrence, is a cyclopentadienyl-moiety-containing group which typically has in the range of 5 to about 24 carbon atoms; B is a bridging group or *ansa* group that links two Cp groups together or alternatively carries an alternate coordinating group such as alkylaminosilylalkyl, silylamido, alkoxy, siloxy, aminosilylalkyl, or analogous monodentate hetero atom electron donating groups; M is a d- or f-block metal atom; each X and each Y is, independently, a group that is bonded to the d- or f-block metal atom; a is 0 or 1; b is a whole integer from 1 to 3 (preferably 2); c is at least 2; d is 0 or 1. The sum of b, c, and d is sufficient to form a stable compound, and often is the coordination number of the d- or f-block metal atom.

[0045] Cp is, independently, a cyclopentadienyl, indenyl, fluorenyl or related group that can π-bond to the metal, or a hydrocarbyl-, halo-, halohydrocarbyl-, hydrocarbylmetalloid-, and/or halohydrocarbylmetalloid-substituted derivative thereof. Cp typically contains up to 75 non-hydrogen atoms. B, if present, is typically a silylene ($-SiR_2-$), benzo ($C_6H_4<$), substituted benzo, methylene ($-CH_2-$), substituted methylene, ethylene ($-CH_2CH_2-$), or substituted ethylene bridge. M is preferably a metal atom of Groups 4-6, and most preferably is a Group 4 metal atom, especially hafnium, and most especially zirconium. X can be a divalent substituent such as an alkylidene group, a cyclometallated hydrocarbyl group, or any other divalent chelating ligand, two loci of which are singly bonded to M to form a cyclic moiety which includes M as a member. Each X, and if present Y, can be, independently in each occurrence, a halogen atom, a hydrocarbyl group (alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, or aralkyl), hydrocarbyloxy, (alkoxy, or aryloxy) siloxy, amino or substituted amino, hydride, acyloxy, triflate, and similar univalent groups that form stable metallocenes. The sum of b, c, and d is a whole number, and is often from 3-5. When M is a Group 4 metal or an actinide metal,

and b is 2, the sum of c and d is 2, c being at least 1. When M is a Group 3 or Lanthanide metal, and b is 2, c is 1 and d is zero. When M is a Group 5 metal, and b is 2, the sum of c and d is 3, c being at least 2.

[0046] Also useful in this invention are compounds analogous to those of Formula (I) where one or more of the Cp groups are replaced by cyclic unsaturated charged groups isoelectronic with Cp, such as borabenzene or substituted borabenzene, azaborole or substituted azaborole, and various other isoelectronic Cp analogs. See for example Krishnamurti, et al., U.S. Pat. No. 5,554,775 and 5,756,611.

[0047] In one preferred group of metallocenes, b is 2, i.e., there are two cyclopentadienyl-moiety containing groups in the molecule, and these two groups can be the same or they can be different from each other.

[0048] Another sub-group of useful metallocenes which can be used in the practice of this invention are metallocenes of the type described in WO 98/32776 published July 30, 1998. These metallocenes are characterized in that one or more cyclopentadienyl groups in the metallocene are substituted by one or more polyatomic groups attached via a N, O, S, or P atom or by a carbon-to-carbon double bond. Examples of such substituents on the cyclopentadienyl ring include -OR, -SR, $-NR_2$, -CH=, -CR=, and $-PR_2$, where R can be the same or different and is a substituted or unsubstituted C_1-C_{16} hydrocarbyl group, a tri-C_1-C_8 hydrocarbylsilyl group, a tri-C_1-C_8 hydrocarbyloxysilyl group, a mixed C_1-C_8 hydrocarbyl and C_1-C_8 hydrocarbyloxysilyl group, a tri-C_1-C_8 hydrocarbylgermyl group, a tri-C_1-C_8 hydrocarbyloxygermyl group, or a mixed C_1-C_8 hydrocarbyl and C_1-C_8 hydrocarbyloxygermyl group.

[0049] Examples of metallocenes to which this invention is applicable include such compounds as:

bis(cyclopentadienyl)zirconium dimethyl;
bis(cyclopentadienyl)zirconium dichloride;
bis(cyclopentadienyl)zirconium monomethylmonochloride;
bis(cyclopentadienyl)titanium dichloride;
bis(cyclopentadienyl)titanium difluoride;
cyclopentadienylzirconium tri-(2-ethylhexanoate);
bis(cyclopentadienyl)zirconium hydrogen chloride;
bis(cyclopentadienyl)hafnium dichloride;
racemic and meso dimethylsilanylene-bis(methylcyclopentadienyl)hafnium dichloride;
racemic dimethylsilanylene-bis(indenyl)hafnium dichloride;
racemic ethylene-bis(indenyl)zirconium dichloride;
(η^5-indenyl)hafnium trichloride;
(η^5-C_5Me_5)hafnium trichloride;
racemic dimethylsilanylene-bis(indenyl)thorium dichloride;

racemic dimethylsilanylene-bis(4,7-dimethyl-1-indenyl)zirconium dichloride;
racemic dimethyl-silanylene-bis(indenyl)uranium dichloride;
racemic dimethylsilanylene-bis(2,3,5-trimethyl-1-cyclopentadienyl)zirconium dichloride;
racemic dimethyl-silanylene(3-methylcyclopentadienyl)hafnium dichloride;
racemic dimethylsilanylene-bis(1-(2-methyl-4-ethyl)indenyl) zirconium dichloride;
racemic dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride;
bis(pentamethylcyclopentadienyl)thorium dichloride;
bis(pentamethylcyclopentadienyl)uranium dichloride;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanetitanium dichloride;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane chromium dichloride;
(tert-butylamido)dimethyl(-η^5-cyclopentadienyl)silanetitanium dichloride;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanemethyltitanium bromide;
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyluranium dichloride;
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride;
(methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylcerium dichloride;
(methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride;
(ethylamido)(tetramethyl-η^5-cyclopentadienyl)methylenetitanium dichloride;
(tert-butylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl)-silanebenzylvanadium chloride;
(benzylamido)dimethyl(indenyl)silanetitanium dichloride;
(phenylphosphido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanebenzyltitaniumchloride;
rac-dimethylsilylbis(2-methyl-1-indenyl)zirconium dimethyl;
rac-ethylenebis(1-indenyl)zirconium dimethyl;
bis(methylcyclopentadienyl)titanium dimethyl;
bis(methylcyclopentadienyl)zirconium dimethyl;
bis(n-butylcyclopentadienyl)zirconium dimethyl;
bis(dimethylcyclopentadienyl)zirconium dimethyl;
bis(diethylcyclopentadienyl)zirconium dimethyl;
bis(methyl-n-butylcyclopentadienyl)zirconium dimethyl;
bis(n-propylcyclopentadienyl)zirconium dimethyl;
bis(2-propylcyclopentadienyl)zirconium dimethyl;
bis(methylethylcyclopentadienyl)zirconium dimethyl;
bis(indenyl)zirconium dimethyl;
bis(methylindenyl)zirconium dimethyl;
dimethylsilylenebis(indenyl)zirconium dimethyl;
dimethylsilylenebis(2-methylindenyl)zirconium dimethyl;
dimethylsilylenebis(2-ethylindenyl)zirconium dimethyl;
dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dimethyl;
1,2-ethylenebis(indenyl)zirconium dimethyl;

1,2-ethylenebis(methylindenyl)zirconium dimethyl;
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)zirconium dimethyl;
dimethylsilylenebis(6-phenylindenyl)zirconium dimethyl;
bis(methylindenyl)zirconium benzyl methyl;
ethylenebis[2-(tert-butyldimethylsiloxy)-1-indenyl] zirconium dimethyl;
dimethylsilylenebis(indenyl)chlorozirconium methyl;
5-(cyclopentadienyl)-5-(9-fluorenyl)1-hexene zirconium dimethyl;
dimethylsilylenebis(2-methylindenyl)hafnium dimethyl;
dimethylsilylenebis(2-ethylindenyl)hafnium dimethyl;
dimethylsilylenebis(2-methyl-4-phenylindenyl)hafnium dimethyl;
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)hafnium dimethyl;
bis(9-fluorenyl)(methyl)(vinyl)silane zirconium dimethyl,
bis(9-fluorenyl)(methyl)(prop-2-enyl)silane zirconium dimethyl,
bis(9-fluorenyl)(methyl)(but-3-enyl)silane zirconium dimethyl,
bis(9-fluorenyl)(methyl)(hex-5-enyl)silane zirconium dimethyl,
bis(9-fluorenyl)(methyl)(oct-7-enyl)silane zirconium dimethyl,
(cyclopentadienyl)(1-allylindenyl) zirconium dimethyl,
bis(1-allylindenyl)zirconium dimethyl,
(9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)zirconium dimethyl,
(9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)zirconium dimethyl,
bis(9-(prop-2-enyl)fluorenyl) zirconium dimethyl,
(9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) zirconium dimethyl,
bis(9-(cyclopent-2-enyl)(fluorenyl)zirconium dimethyl,
5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene zirconium dimethyl,
1-(9-fluorenyl)-1-(cyclopentadienyl)-1-(but-3-enyl)-1-(methyl)methane zirconium dimethyl,
5-(fluorenyl)-5-(cyclopentadienyl)-1-hexene hafnium dimethyl,
(9-fluorenyl)(1-allylindenyl)dimethylsilane zirconium dimethyl,
1-(2,7-di(alpha-methylvinyl)(9-fluorenyl)-1-(cyclopentadienyl)-1,1-dimethylmethane zirconium dimethyl,
1-(2,7-di(cyclohex-1-enyl)(9-fluorenyl))-1-(cyclopentadienyl)-1,1-methane zirconium dimethyl,
5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dimethyl,
5-(cyclopentadienyl)-5-(9-fluorenyl)1-hexene titanium dimethyl,
bis(9-fluorenyl)(methyl)(vinyl)silane titanium dimethyl,
bis(9-fluorenyl)(methyl)(prop-2-enyl)silane titanium dimethyl,
bis(9-fluorenyl)(methyl)(but-3-enyl)silane titanium dimethyl,
bis(9-fluorenyl)(methyl)(hex-5-enyl)silane titanium dimethyl,
bis(9-fluorenyl)(methyl)(oct-7-enyl)silane titanium dimethyl,

(cyclopentadienyl)(1-allylindenyl) titanium dimethyl,
bis(1-allylindenyl)titanium dimethyl,
(9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)hafnium dimethyl,
(9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)hafnium dimethyl,
bis(9-(prop-2-enyl)fluorenyl) hafnium dimethyl,
(9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) hafnium dimethyl,
bis(9-(cyclopent-2-enyl)(fluorenyl)hafnium dimethyl,
5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene hafnium dimethyl,
5-(fluorenyl)-5-(cyclopentadienyl)-1-octene hafnium dimethyl,
(9-fluorenyl)(1-allylindenyl)dimethylsilane hafnium dimethyl.
(tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium(1,3-pentadiene);
(cyclopentadienyl)(9-fluorenyl)diphenylmethane zirconium dimethyl;
(cyclopentadienyl)(9-fluorenyl)diphenylmethane hafnium dimethyl;
dimethylsilanylene-bis(indenyl) thorium dimethyl;
dimethylsilanylene-bis(4,7-dimethyl-1-indenyl) zirconium dimethyl;
dimethylsilanylene-bis(indenyl) uranium dimethyl;
dimethylsilanylene-bis(2-methyl-4-ethyl-1-indenyl) zirconium dimethyl;
dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dimethyl;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane titanium dimethyl;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane chromium dimethyl;
(tert-butylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane titanium dimethyl;
(phenylphosphido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane titanium dimethyl; and
[dimethylsilanediylbis(indenyl)]scandium methyl.

In many cases the metallocenes such as referred to above will exist as racemic mixtures, but pure enantiomeric forms or mixtures enriched in a given enantiomeric form can be used.

[0050] Other organometallic catalytic compounds with which the hydrocarbylhaloaluminoxanes of this invention can be used in forming novel catalysts of this invention are the late transition metal catalyst described, for example, in U.S. Pat. Nos. 5,516,739 to Barborak, et al.; 5,561,216 to Barborak, et al.; 5,866,663 to Brookhart, et al; 5,880,241 to Brookhart, et al; and 6,114,483 to Coughlin, et al. Such catalysts are sometimes referred to herein collectively as "a Brookhart-type late transition metal catalyst compound or complex".

[0051] Other transition metal catalyst compounds and catalyst complexes that can be used in the practice of this invention include cationic nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands such as described in Johnson et al. WO 96/23010; palladium and nickel catalysts containing selected bidentate phosphorus-containing ligands such as described in EP 381,495; cationic α-diimine-based nickel and palladium complexes such as described by Johnson et al. in *J. Am. Chem. Soc.*, **1995**, *117*, 6414, see also

Brown et al. WO 97/17380; nickel complexes such as described by Johnson et al. in U.S. Pat. No. 5,714,556; cobalt(III) cyclopentadienyl catalytic systems such as described by Schmidt et al. in *J. Am. Chem. Soc.*, **1985**, *107*, 1443, and by Brookhart et al. in *Macromolecules*, **1995**, *28*, 5378; anionic phosphorus, oxygen donors ligated to nickel(II) such as described by Klabunde in U.S. Pat Nos. 4,716,205, 4,906,754, 5,030,606, and 5,175,326; Group 8-10 transition metal complexes coordinated with a bidentate ligand such as described in WO 98/40374; transition metal complexes with bidentate ligands containing pyridine or quinoline moieties such as described in U.S. Pat. No. 5,637,660; quinolinoxy or pyridinoxy-substituted Group 4 transition metal trihalides such as described in U.S. Pat. No. 6,020,493; nickel complexes such as described by bis(ylide)nickel complexes such as described by Starzewski et al. in *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 63, and U.S. Pat. No. 4,691,036; neutral N, O, P, or S donor ligands in combination with a nickel(O) compound and an acid such as described in WO 97/02298; aminobis(imino)phosphorane nickel catalysts such as described by Fink et al. in U.S. Pat. No. 4,724,273.

[0052] Illustrative, non-limiting additional examples of various types of transition metal compounds that can be employed include the following:

2,6-bis-[1-(1-methylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis[1-(1-ethylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis[1-(1-isopropylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis-(1-(2-methylphenylimino)ethyl)pyridine iron(II) chloride;

N,N'-di(trimethylsilyl)benzamidinato copper(II);

tridentate Schiff base complexes of cobalt and iron described by Mashima in *Shokubai* **1999**, vol. *41*, p. 58;

nickel compounds of the type described in U. S. Patent 5,880,323;

nickel(II) acetylacetonate;

bis(acetonitrile)dichloro palladium(II);

bis(acetonitrile)bis(tetrafluoroborate)palladium(II);

(2,2'-bipyridine)dichloro palladium(II);

bis(cyclooctadienyl) nickel(0);

palladium(II) acetylacetonate;

bis(salicylaldiminato) complexes of the type described by Matsui *et. al.* in *Chemistry Letters* **2000**, pp. 554-555;

cobalt dioctoate;

cobaltocene;

(cyclopentadienyl)(triphenylphosphino)cobalt(II) diiodide; and

nickel compounds of the type described in JP 09-272709.

[0053] Preferred transition metal compounds which can be used in forming the catalysts of this invention are transition metal compounds which can be represented by the formula:

$$MX_nY_m$$

where M is a transition metal of Group 3 to 11 including the lanthanide series and actinide series, and preferably is a transition metal of Group 4, 5, 8, 9, or 10 of the Periodic Table or is copper, and Y is, independently, a halide or pseudohalide, n is the valence of M, and m is an integer of from 0 to n-1. Of the pseudohalides, preferred are alkoxide or oxyhalide groups. Pseudohalides, which is a term of art, refers to anionic moieties which as salt-like anions which are non-halogenides. Non-limiting examples of suitable pseudohalide groups are oxyhalide groups, hydrocarbyloxy groups (-OR groups such as alkoxy, aryloxy, cycloalkoxy, or arylalkoxy), amido groups ($-NR_2$), hydrocarbylthio groups (-SR groups). Most preferred are compounds of the above formula wherein M is a Group 4 metal. Non-limiting examples of suitable transition metal compounds include, for example, transition metal halides and oxyhalides such as titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride, titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, hafnium oxychloride, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium triiodide, vanadium oxytrichloride, vanadium oxytribromide, niobium pentabromide, niobium pentachloride, niobium pentafluoride, tantalum pentabromide, tantalum pentachloride, tantalum pentafluoride, chromous bromide, chromic bromide, chromous chloride, chromic chloride, chromous fluoride, chromic fluoride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide, molybdenum dichloride, molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, molybdenum hexafluoride, lanthanum trichloride, cerous fluoride, cerous chloride, cerous bromide, cerous iodide, ceric fluoride, uranium trichloride, uranium tetrachloride, uranium tribromide, uranium tetrabromide, thorium tetrachloride, thorium tetrabromide. Among suitable alkoxides and mixed halide/alkoxides of the transition metals are $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(O\text{-iso-}C_3H_7)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(O\text{-iso-}C_3H_7)_2Cl_2$, $Ti(OC_{17}H_{18})_2Br_2$, $Zr(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $Zr(OC_5H_{11})_4$, $ZrCl_3(OC_2H_5)$, $ZrCl(OC_4H_9)_3$, $Hf(OC_4H_9)_4$, $Hf(OC_4H_9)_3Cl$, $VO(OC_2H_5)_3$, $Cr(O\text{-iso-}C_4H_9)_3$, $Mo(OC_2H_5)_3$. Other transition metal compounds which may be used include amides such as $Ti(NMe_2)_4$, $Zr(NMe_2)_4$, $Ti(NEt_2)_4$, $Zr(NEt_2)_4$, and $Ti(NBu_2)_4$; carboxylic acid salts such as titanium oxalate, cobalt acetate, chromium acetate, nickel formate, thallium oxalate, and uranyl formate. Among the more preferred transition metal compounds are the halides, oxyhalides, alkoxides, and mixed halide-alkoxides of the Group 4 to 6 metals, and more particularly of the metals of Groups 4 and 5. Among especially preferred transition metal compounds are the trivalent

or tetravalent Group 4 metal halides, particularly the chlorides, and the vanadium oxyhalides, particularly vanadium oxytrichloride. The Periodic Table referred to is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*.

[0054] Supported catalysts of this invention can be prepared by combining in any order the transition metal compound, a hydrocarbylhaloalumoxane, and the support in one or more suitable solvents or diluent. Suitable solvents and/or diluents include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcyclopentane; and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene. Mixtures of different types of such hydrocarbons can also be used, such as a mixture of one or more acyclic aliphatic hydrocarbons and one or more cycloaliphatic hydrocarbons; a mixture of one or more acyclic aliphatic hydrocarbons and one or more aromatic hydrocarbons; a mixture of one or more cycloaliphatic hydrocarbons and one or more aromatic hydrocarbons; or a mixture of one or more acyclic aliphatic hydrocarbons, one or more cycloaliphatic hydrocarbons, and one or more aromatic hydrocarbons.

[0055] It is preferred that the catalyst components as well as the resultant catalyst compositions be handled in an inert, moisture-free, oxygen free environment such as argon, nitrogen or helium because of the sensitivity of the catalyst components and catalyst compositions to moisture and oxygen.

[0056] In one method of forming the catalyst composition, the transition metal compound and hydrocarbylhaloaluminoxane are combined in a first step in a suitable solvent such as an aromatic solvent to produce a solution of the reaction product. This reaction may be carried out at one or more suitable temperatures within the range of about -100 to about 300°C., preferably about 0 to about 100°C. Holding times to allow for the completion of the reaction may range from about 10 seconds to about 60 minutes depending on the reaction variables. The solution produced by combining the transition metal compound and hydrocarbylhaloaluminoxane is then contacted with the support. The method of contact may vary, but it is preferred that the support be added to the catalyst solution with vigorous stirring. Again contact temperatures may range from about 0 to about 100°C depending upon the solvents used. Contact times may vary from about 10 seconds to about 60 minutes or longer. The solvent can then be removed, typically by applying a vacuum. The solution may or may not be heated in order to aid in the removal of the solvent.

[0057] A preferred method of forming the catalyst compositions of this invention comprises forming the hydrocarbylhaloaluminoxane by controlled hydrolysis of the hydrocarbylaluminum halide starting material in the presence of the inorganic catalyst support such as silica, alumina, silica-alumina, or other inorganic oxide-type catalyst support material, for example as a slurry in a suitable inert diluent; and contacting the resultant supported

hydrocarbylhaloaluminoxane -- preferably after separation from the hydrolysis reaction mixture and washing with an inert solvent or diluent -- with or in a solution of the transition metal compound in a suitable anhydrous inert solvent, preferably with agitation. In this way the hydrocarbylhaloaluminoxane and the transition metal compound can interact to produce an active supported catalyst composition.

[0058] Regardless of the method used in the preparation, the active supported catalyst can be recovered by evaporation of the solvent to obtain a free-flowing solid or alternatively, the active supported catalyst can be maintained in its slurry state for direct use. Another variant is to replace the original solvent/diluent with another inert liquid diluent such as a paraffinic hydrocarbon to thereby provide a slurry of active catalyst for use in the polymerization.

[0059] Modified supported catalysts of this invention can be prepared by combining in any order at least one transition metal compound, at least one hydrocarbylhaloalumoxane component, at least one modifier, and the support in one or more suitable solvents or diluents. A modifier may be defined as a compound containing a Lewis acid or basic functionality, such as, for example, tetraethoxysilane, phenyltri(ethoxy)silane, bis-tert-butylhydroxytoluene (BHT), N,N-dimethylaniline. Suitable solvents and/or diluents are the same as those described above. It is preferred that these catalyst components be handled in an inert, moisture-free, oxygen-free environment such as argon, nitrogen or helium because of the sensitivity of the catalyst components to moisture and oxygen.

[0060] In a preferred method of forming a modified supported catalyst, the hydrocarbylhaloaluminoxane and the modifier are combined in a first step in a suitable solvent such as an aromatic solvent to produce a solution or slurry. The transition metal compound is then added to this solution. These combined steps may be carried out in the temperature range of about -100 to about 300°C, and preferably in the range of about 0 to about 100°C. Holding times to allow for the completion of the reaction may range from about 10 seconds to about 60 minutes depending on the reaction variables. The solution produced by combining the transition metal compound, the hydrocarbylhaloalumoxane and the modifier can then be contacted with the support, or preferably the hydrocarbylhaloalumoxane is in the presence of the support as formed and thus is supported on the inorganic catalyst support *ab initio*. This supported hydrocarbylhaloalumoxane is then treated with the modifier and then with the transition metal compound in a suitable inert organic medium such as an aromatic solvent to produce a slurry of active modified catalyst of this invention. In these operations contact temperatures may range from about 0 to about 100°C depending upon the solvents used. Contact times may vary from about 10 seconds to about 60 minutes or longer.

[0061] Regardless of the method used in forming the modified catalyst, the solvent or diluent can be removed, typically by applying a vacuum, in order to isolate the catalyst. The solution may or may not be heated in order to aid in the removal of the solvent. Alternatively the active catalyst slurry, with some of the solvent/diluent stripped away if desired, can be

used as a component in conducting the polymerization. Another variant is to replace the original solvent/diluent with another inert liquid diluent such as a paraffinic hydrocarbon to thereby provide a slurry of active catalyst for use in the polymerization.

[0062] In accordance with this invention, optimum results are generally obtained wherein the molar ratio of hydrocarbylhaloalumoxane to transition metal compound is from about 1.1 to about 20,000:1, preferably from about 10:1 to about 1000:1, and the molar ratio of hydrocarbylhaloalumoxane to modifier is from about 1:1 to about 20,000:1, preferably from about 10:1 to about 1000:1. The concentration of transition metal compound on the support is typically between 0.001 wt% and about 10 wt%, desirably between 0.01 wt% and about 10 wt%, and preferably about 0.1 wt% to about 10 wt% based upon the weight of the support.

[0063] The supported catalyst systems of this invention are useful in producing olefin polymers and especially ethylene polymers, propylene polymers, ethylene/α-olefin copolymers, styrene polymers and copolymers.

[0064] In conducting the polymerizations pursuant to this invention, the catalyst components can be used in solution or deposited on a solid support. When used in solution polymerization, the solvent can be, where applicable, a large excess quantity of the liquid olefinic monomer. Typically, however, an ancillary inert solvent, typically a liquid paraffinic or aromatic hydrocarbon solvent is used, such as heptane, isooctane, decane, toluene, xylene, ethylbenzene, mesitylene, or mixtures of liquid paraffinic hydrocarbons and/or liquid aromatic hydrocarbons.

[0065] Polymers can be produced pursuant to this invention by homopolymerization of olefins, typically 1-olefins (also known as α-olefins) such as ethylene, propylene, 1-butene, styrene, or copolymerization of two or more copolymerizable monomers, at least one of which is typically a 1-olefin. The other monomer(s) used in forming such copolymers can be one or more different 1-olefins and/or a diolefin, and/or a acetylenic monomer. Olefins that can be polymerized in the presence of the catalyst compositions of this invention include α-olefins having 2 to 20 carbon atoms such as ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. Normally, the hydrocarbon monomers used, such as 1-olefins, diolefins and/or acetylene monomers, will contain up to about 10 carbon atoms per molecule. Preferred 1-olefin monomers for use in the process include ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. It is particularly preferred to use supported or unsupported catalysts of this invention in the polymerization of ethylene, or propylene, or ethylene and at least one C_3-C_8 1-olefin copolymerizable with ethylene. Typical diolefin monomers which can be used to form terpolymers with ethylene and propylene include butadiene, hexadiene, norbornadiene, and similar copolymerizable diene hydrocarbons. 1-Heptyne and 1-octyne are illustrative of suitable acetylenic monomers which can be used.

[0066] Often the monomer used is a 1-alkene monomer whereby a homopolymer is prepared. In other frequent cases a mixture of a 1-alkene monomer such as ethylene and at least one monomer copolymerizable therewith is used whereby a copolymer is produced.

[0067] Polymerization of ethylene or copolymerization with ethylene and an α-olefin having 3 to 10 carbon atoms may be performed in either the gas or liquid phase (*e.g.*, in a solvent, such as toluene, or heptane). The polymerization can be conducted at conventional temperatures (*e.g.*, 0° to 120°C.) and pressures (*e.g.*, ambient to 50 kg/cm^2) using conventional procedures as to molecular weight regulations.

[0068] The heterogeneous catalysts of this invention can be used in polymerizations conducted as slurry processes or as gas phase processes. By "slurry" in this connection is meant that the particulate catalyst is used as a slurry or dispersion in a suitable liquid reaction medium which may be composed of one or more ancillary solvents (*e.g.*, liquid aliphatic or aromatic hydrocarbons) or an excess amount of liquid monomer to be polymerized in bulk. Generally speaking, these polymerizations are conducted at one or more temperatures in the range of about 0 to about 160°C and under atmospheric, subatmospheric, or superatmospheric conditions. Preferably polymerizations conducted in a liquid reaction medium containing a slurry or dispersion of a catalyst of this invention are conducted at temperatures in the range of about 40 to about 110°C. Typical liquid diluents for such processes include isobutane, pentane, isopentane, hexane, heptane, toluene, and like materials. Typically, when conducting gas phase polymerizations, superatmospheric pressures are used, and the reactions are conducted at temperatures in the range of about 50 to about 160°C. These gas phase polymerizations can be performed in a stirred or fluidized bed of catalyst in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated to maintain the particles at the desired polymerization reaction temperature. An aluminum alkyl such as triethylaluminum may be added as a scavenger of water, oxygen and other impurities. In such cases the aluminum alkyl is preferably employed as a solution in a suitable dry liquid hydrocarbon solvent such as toluene or xylene. Concentrations of such solutions in the range of about 5×10^{-5} molar are conveniently used. But solutions of greater or lesser concentrations can be used, if desired. Polymer product can be withdrawn continuously or semi-continuously at a rate that maintains a constant product inventory in the reactor.

[0069] In general, the polymerizations and copolymerizations conducted pursuant to this invention are carried out using a catalytically effective amount of a novel catalyst composition of this invention, which amount may be varied depending upon such factors such as the type of polymerization being conducted, the polymerization conditions being used, and the type of reaction equipment in which the polymerization is being conducted. In many cases, the amount of the catalyst of this invention used will be such as to provide in the range of about

0.000001 to about 0.01 percent by weight of transition, lanthanide, or actinide metal based on the weight of the monomer(s) being polymerized.

[0070] After polymerization and deactivation of the catalyst in a conventional manner, the product polymer can be recovered from the polymerization reactor by any suitable means. When conducting the process with a slurry or dispersion of the catalyst in a liquid medium the product typically is recovered by a physical separation technique (*e.g.*, decantation). The recovered polymer is usually washed with one or more suitably volatile solvents to remove residual polymerization solvent or other impurities, and then dried, typically under reduced pressure with or without addition of heat. When conducting the process as a gas phase polymerization, the product after removal from the gas phase reactor is typically freed of residual monomer by means of a nitrogen purge, and may possibly be used without further catalyst deactivation or catalyst removal.

[0071] When preparing polymers pursuant to this invention conditions may be used for preparing unimodal or multimodal polymer types. For example, mixtures of catalysts of this invention formed from two or more different metallocenes having different propagation and termination rate constants for ethylene polymerizations can be used in preparing polymers having broad molecular weight distributions of the multimodal type. The following examples illustrate this invention by presentation of preferred embodiments thereof. All experiments of these Examples were carried out under inert atmosphere conditions, using Schlenk glassware and vacuum line, in conjunction with a nitrogen drybox. Solvents were dried using standard methods. Filtration and vacuum distillation were done inside the nitrogen drybox and distillates collected in a trap at -78°C. Alkylaluminum halides were obtained from stock solutions manufactured by Albemarle Corporation. Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) was purchased from Strem Chemical Company. Fifty weight percent solutions of dimethylaluminum chloride (DMAC, 5.4 mmol Al/g) and of diethylaluminum chloride (DEAC, 4.15 mmol Al/g) were kept in the nitrogen box as stock solutions. The hydrolysis ratios given in the Examples are moles of Al (as R_2AlX) to moles of water (as $LiOH{\bullet}H_2O$).

EXAMPLE 1

Preparation of C-MAO

[0072] DMAC stock solution (31.5g, 170 mmol Al) was further diluted with toluene (150mL). This solution was treated with $LiOH.H_2O$ (LHM, 7.14g, 170 mmol, hydrolysis ratio 1:1) in three equal batches with vigorous stirring inside the nitrogen purge box. An interval of about one hour was allowed between each solid addition. The reaction was exothermic with obvious gas evolution. After all the LHM had been added, the reactions mixture was stirred for an additional 3 hours. The mixture was filtered through a medium frit. Clear and colorless filtrate (157.6g) which contained greater than 90 percent of the original aluminum value was obtained. The liquid product, (chloro)(methyl)aluminoxane (C-MAO) was stored

in a reaction bottle and kept at room temperature in a nitrogen drybox. After about 2 days, some crystalline material began to grow from the liquid product. Within 2 weeks, a quantitative amount of crystalline product was obtained. Some of the crystalline material was successfully analyzed by X-ray structural analysis. This revealed an unprecedented 16-aluminum crystalline cluster having the general formula $Me_9Al_{16}O_{13}Cl_{13}$. This crystalline C-MAO product:

$$[Me_3Al_3Cl_2O]_3[O_3AlCl][(ClAlO)_6O]$$

crystallizes in the trigonal space group R3m with a = 21.1316 (7), b = 21.1316 (7), c = 10.5050 (4) A, V = 4062.5 (2) A^3 for Z = 3. Least-square refinement based on 2049 observed reflections converged at R = 0.048 (R_w = 0.144). The molecule possesses a central core structure consisting of three fused hexagonal rings, $[(ClAlO)_6)O]$. The whole molecule resides on a threefold axis, which passes through the unique Cl-Al bond and the center of the core structure. The central core structure could also be viewed as $[Cl_2AlO_2]_3[Al_3O]$. Fig. 1 depicts a view of the X-ray crystallographic structure of the compound through the unique 3-fold axis of symmetry of Cl-Al bond.

EXAMPLE 2

Preparation of C-EAO

[0073] DEAC stock solution (30.4g, 126.1 mmol Al) was further diluted with toluene (100 mL) and then treated with LHM (5.29g, 126.1 mmol, hydrolysis ratio 1:1) in two batches with an hour interval between additions. Initially, the reaction was barely exothermic, but became more exothermic later. After addition, the reaction mixture was stirred for a total reaction time of 6 hours. Clear and colorless reaction product (100.1g) was obtained after filtration through a medium frit. The liquid product, (chloro)(ethyl)aluminoxane (C-EAO) was stored in a clear reaction bottle. On standing at room temperature in the nitrogen drybox, a quantitative amount of crystalline product was formed within a period of two weeks. Surprisingly, X-ray structural analysis of the crystalline product revealed that it is isostructural with C-MAO.

EXAMPLE 3

[0074] DMAC stock solution (30.25 g, 163.4 mmol Al) was treated with LHM (5.15g, 122.5 mmol, hydrolysis ratio 1:0.75), but otherwise as described in Example 1. The clear and colorless liquid product was placed in a clear reaction bottle stored at room temperature in a nitrogen drybox. After about 3 weeks, only a few crystals of a crystalline product formed. This is unlike Example 1 where crystal formation was quantitative.

EXAMPLE 4

[0075] DEAC stock solution (31.0g, 128.6 mmol Al) was treated with LHM (4.32g, 102.8

mmol, hydrolysis ratio 1:0.8), but otherwise as described in Example 2. The product was stored at room temperature in N_2 drybox. After about 4 weeks, significantly lesser amount of crystalline material compared to Example 2 was obtained.

EXAMPLE 5

[0076] It is generally known that dimeric alkylaluminoxane or alkylhaloaluminoxane are prepared by hydrolyzing the corresponding alkylaluminum compound in a 2:1 ratio (or 1:0.5, $Al:H_2O$). Accordingly, DEAC stock solution (30.69g, 127.27 mmol Al) further diluted with toluene (30g) was treated with LHM (2.7g, 63.6 mmol, hydrolysis ratio 1:0.5), but otherwise as described in Example 2. Gas evolution was apparent but the reaction was only mildly exothermic. The resulting solution product was stable to crystal formation at room temperature -- no visible crystalline product could be seen even after 4 weeks.

EXAMPLE 6

[0077] DMAC stock solution (38.2g, 206.28 mmol Al) was further diluted with toluene (38g) and then treated with LHM (4.3g, 103.1 mmol, hydrolysis ratio 1:0.5) as described in Example 1. The resulting solution product was stable to crystal formation at room temperature even after 4 weeks.

EXAMPLE 7

Preparation of Silica Supported C-MAO and C-MAO/SIL

[0078] A) Silica particles were initially dried at 600°C and then stored under nitrogen. DMAC stock solution (30.16g, 162.9 mmol Al) was further diluted with toluene (150 mL). The DMAC solution was treated with LHM (6.84g, 162.9 mmol, hydrolysis ratio 1:1) in three batches as described in Example 1. The resulting solution product (148.5g) was clear and colorless. An aliquot of the solution product (C-MAO, 70g) was treated with dried silica (7.4g) in batches and kept at room temperature overnight. NMR of the supernatant liquid showed that only about 50 percent of the initial aluminum value was absorbed into the silica. The slurry was heated at 70°C for 3 hours. NMR showed no change. Then more silica (7.4g) was added and the mixture kept at room temperature overnight. NMR of the supernatant liquid showed the absence of Al-Me groups. Therefore, all the C-MAO product had been absorbed into the silica. The mixture was filtered through a medium first. The solid supported product was washed with toluene (3x50mL). This solid product was dried under vacuum in the N_2 drybox for 2 hours resulting in a colorless solid product.

[0079] B) To ensure that all solvent had been removed, the solid was transferred into a Schlenk flask and left under reduced pressure overnight. Surprisingly, a yellowish solid product resulted. This was surprising, given that the C-MAO solution and also the initially-dried silica product were both colorless. Under vacuum, the yellowish solid product was

further heated at 60°C for another one hour period. The yellowish solid product (C-MAO/SIL) was sent for analysis and found to afford quantitative recovery of the initial aluminum value. It is evident, therefore, that the C-MAO and the silica chemically interacted with each other to produce a new yellowish substance, C-MAO/SIL.

[0080] C) After about 3 weeks, the remaining initial solution product of Example 7 developed quantitative precipitation of crystalline product, which has similar NMR pattern as observed for the crystalline product of Example 1.

[0081] The reaction product (C-MAO/SIL) of part B) of Example 7 could be referred to as supported C-MAO on silica, but this would obscure the true significance of the observed color change indicative of an actual reaction process and product. In general, the term, "silica supported haloaluminoxane" refers to haloaluminoxane compositions of this invention that have been physically absorbed or adsorbed into the silica pores or surfaces, e.g., as in part A) of Example 7, without an apparent chemical reaction between the aluminoxane and silica. Accordingly the term "(chloro)(methyl)aluminoxane/silica product" or "C-MAO/SIL" has been applied to this particular new product of this invention. Other analogous products of this invention would be named analogously, and generically this class of products can be named as "hydrocarbylhaloaluminoxane/silica products".

EXAMPLE 8

NMR (Nuclear Magnetic Resonance) Experiments

[0082] In general, aluminoxanes and previously-known haloaluminoxanes are known to be oligomers that usually exhibit characteristic complex broad peaks both in ^{1}H and ^{27}Al NMR. Surprisingly, C-MAO and C-EAO of the present invention showed relatively simple NMR peaks which are uncharacteristically sharp compared to hitherto known aluminoxane compositions. The discrete nature of C-MAO and C-EAO of this invention is further confirmed by the observation of 3 sharp peaks both in solution and solid ^{27}Al NMR experiments.

EXAMPLE 9

Preparation of Supported Catalyst System Using C-MAO/SIL

[0083] The yellowish reaction product between C-MAO and silica, as described in Example 7, was used to produce a silica supported catalyst system. C-MAO/SIL (5g, 14.8 mmol Al) was placed in a reaction bottle. Titanium tetrachloride ($TiCl_4$, 1g) was diluted with toluene to 15 g solution. This yellowish solution was slowly added to the solid C-MAO/SIL. A brown slurry formed immediately. The mixture was kept at room temperature overnight. Then the slurry was heated at 80°C for 2 hours. The slurry became slightly darker brown. Upon filtration followed by washing with toluene (3x10mL) and cyclohexane (3x10 mL), a yellowish brown solid composition (C-MAO/SIL/$TiCl_4$) was obtained. The solid was further

dried under reduced pressure and sent for analysis. The product analyzed for 7.7 wt% Al and 0.84 wt% Ti which is approximately Al/Ti ratio of 16. It is important to note that the crystalline C-MAO product contains 16 aluminum atoms ($Me_9Al_{16}O_{13}Cl_{13}$) as per X-ray structural analysis. Since C-MAO/SIL/$TiCl_4$ analysis also indicates Al/Ti ratio of 16, it appears and it is believed that one mole of C-MAO actually reacts with one mole of $TiCl_4$ to form this composition. This is indicative of a stoichiometric reaction which hitherto is rather unheard of in aluminoxane activator chemistry.

EXAMPLE 10

Olefin Polymerizations

[0084] Ethylene polymerization runs were performed in a 1L reactor under mild conditions of 60°C and 130 psi in isobutane solution using the silica-supported catalyst system of Example 9. Under these conditions, the average productivity was 7000 g/g cat/h. Four identical ethylene polymerization runs were conducted differing only in that the length of the polymerizations were for 15, 20, 25 and 30 minutes, respectively. GPC showed polyethylene Mw values of 453,000 to 1,154,000.

[0085] Silica-supported haloaluminoxanes of this invention (i.e., where no apparent chemical reaction has occurred between the hydrocarbylhaloaluminoxane and the silica) are also capable of producing active polymerization catalysts with transition metal catalyst compounds such as, for example, the Group 4-8 metal halides, pseudohalides, alkoxides or mixed halide-alkoxides described above.

[0086] In summary, some of the embodiments of this invention are as follows:

A) Each and every hydrocarbylhaloaluminoxane compound of this invention.

B) Each and every method of this invention for preparing a hydrocarbylhaloaluminoxane compound of this invention.

C) A catalyst composition which comprises a composition formed from interaction between components comprising (i) a hydrocarbylhaloaluminoxane compound of this invention, and (ii) at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series.

D) A composition as in C) wherein component (i) is supported on an organic or inorganic catalyst support or carrier.

E) A composition as in C) wherein the catalyst composition is supported on an organic or inorganic catalyst support or carrier.

F) A composition as in D) or E) wherein the catalyst support or carrier is an inorganic support or carrier.

G) A composition as in F) wherein the inorganic support or carrier is at least one inorganic oxide, a magnesium halide, or a zeolite catalyst support or carrier.

H) A composition as in F) wherein the inorganic support or carrier is a silica, alumina,

or silica-alumina catalyst support or carrier.

I) A catalyst composition which comprises a composition formed from interaction between components comprising (i) a hydrocarbylhaloaluminoxane compound of this invention wherein the composition while on a catalyst support or carrier has been converted under reduced pressure to a composition having a change in color, and (ii) at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series.

J) A composition as in I) wherein the catalyst support is an inorganic catalyst support or carrier.

K) A composition as in J) wherein the inorganic support or carrier is a zeolite, magnesium halide, silica, alumina, silica-alumina, or refractory clay catalyst support or carrier.

L) A composition as in J) wherein the inorganic support or carrier is an inorganic oxide support or carrier.

M) A composition as in L) wherein the inorganic support or carrier is a silica support or carrier.

N) A method of producing a supported catalyst composition, which method comprises
   a) subjecting a dihydrocarbylaluminum halide to controlled partial hydrolysis in an inert diluent in the presence of a catalyst support or carrier to form a supported composition in which a hydrocarbylhaloaluminoxane compound of this invention is supported on the catalyst support or carrier; and
   b) contacting such supported composition with at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series to form a supported catalyst composition.

O) A method of producing a supported catalyst composition, which method comprises
   a) subjecting a dihydrocarbylaluminum halide to controlled partial hydrolysis in an inert diluent in the presence of a catalyst support or carrier to form a supported composition in which a hydrocarbylhaloaluminoxane compound of this invention is supported on the catalyst support or carrier;
   b) recovering such supported composition and subjecting the supported composition to reduced pressure such that the composition on the support is converted to a supported composition having a change in color; and
   c) contacting such supported composition having a change in color with at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series to form a supported catalyst composition.

P) A method of producing a supported catalyst composition, which method comprises
   a) subjecting a dihydrocarbylaluminum halide to controlled partial hydrolysis in

an inert diluent to form a liquid reaction mixture, and bringing a catalyst support or carrier into contact with such reaction mixture during or after completion of the partial hydrolysis but before any substantial crystal formation takes place in such reaction mixture, to form a supported composition in which a hydrocarbylhaloaluminoxane compound of this invention is supported on such catalyst support or carrier; and

b) contacting such supported composition with at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series to form a supported catalyst composition.

Q) A method of producing a supported catalyst composition, which method comprises

a) subjecting a dihydrocarbylaluminum halide to controlled partial hydrolysis in an inert diluent to form a liquid reaction mixture, and bringing a catalyst support or carrier into contact with the reaction mixture during or after completion of such partial hydrolysis but before any substantial crystal formation takes place in the reaction mixture, to form a supported composition in which a hydrocarbylhaloaluminoxane compound of this invention is supported on such catalyst support or carrier;

b) recovering such supported composition and subjecting the supported composition to reduced pressure such that the composition on such support is converted to a supported composition having a change in color; and

c) contacting such supported composition having a change in color with at least one catalyst compound or complex of a transition metal of Groups 3 to 11 including the lanthanide series and the actinide series to form a supported catalyst composition.

R) A method as in any of N), O), P, or Q) wherein free water or a metal hydrate is used to effect the controlled partial hydrolysis.

S) A method as in any of N), O), P, or Q) wherein lithium hydroxide monohydrate is used to effect the controlled partial hydrolysis.

[0087] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another reactant, or a solvent). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical operation or reaction or in forming a mixture to be used in conducting a desired

operation or reaction. Also, even though an embodiment may refer to substances, components and/or ingredients in the present tense (e.g., "is comprised of", "comprises", or "is"), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0088] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

CLAIMS:

1. A discrete hydrocarbylhaloaluminoxane compound having a molecular weight of above 1000 and a defined ratio of hydrocarbyl groups, aluminum atoms, and oxygen atoms in the molecule.

2. A compound of claim 1 further characterized by having an X-ray crystal structure.

3. A compound of claims 1 or 2 having a cluster of fused hexagonal rings having the formula $[(XAlO)_6O]$ where R is a hydrocarbyl group, and X is a halogen atom.

4. A compound of claims 1 or 2 having the formula:

$$R_9Al_{16}O_{13}X_{13}$$

where R is a hydrocarbyl group and X is a halogen atom.

5. A compound of claims 1 or 2 having the formula:

$$[R_3Al_3X_2O]_3[O_3AlX][(XAlO)_6O]$$

where R is a hydrocarbyl group and X is a halogen atom.

6. A compound of any of claims 3-5 wherein X is a fluorine or chlorine atom.

7. A compound of claim 6 wherein X is a chlorine atom.

8. A compound of any of claims 3-6 wherein R is methyl.

9. A compound of any of claims 3-6 wherein R is ethyl.

10. A compound of claim 2 of the formula

$$[R_3Al_3Cl_2O]_3[O_3AlCl][(ClAlO)_6O]$$

where R is methyl or ethyl.

11. A composition which comprises a compound of any of claims 1-10 supported on an inorganic or organic catalyst support or carrier.

12. A composition of claim 11 wherein said support or carrier is an inorganic catalyst support or carrier.

13. A composition of claim 12 wherein said inorganic support or carrier is comprised of a zeolite, magnesium chloride, or at least one inorganic oxide.

14. A composition of claim 12 wherein said inorganic support or carrier is silica, alumina, or silica-alumina.

15. A composition of claim 12 wherein said inorganic support or carrier is silica, and wherein said composition has been converted under reduced pressure to a composition having a change in color.

16. A method which comprises subjecting a hydrocarbylaluminum halide to controlled partial hydrolysis with water as free water or as a metal hydrate in a molar ratio of water as free water or as a metal hydrate to the particular hydrocarbylaluminum halide being used that forms a compound of any of claims 1-5.

17. A method of claim 16 wherein said hydrocarbylaluminum halide is a dialkylaluminum fluoride or chloride so that a compound of any of claims 3-6 is formed in which R is alkyl and X is F or Cl.

18. A method of claim 16 wherein said hydrocarbylaluminum halide is a dialkylaluminum chloride in which the alkyl is methyl or ethyl so that a compound of any of any of claims 3-10 is formed in which R is methyl or ethyl and X is Cl.

19. A method of any of claims 16-18 wherein the controlled hydrolysis is effected by use of lithium hydroxide monohydrate.

20. A method of producing a supported hydrocarbylhaloaluminoxane composition, which method comprises performing the method of any of claims 16-18 in an inert diluent;

A) in the presence of an organic or inorganic catalyst support or carrier to form the supported hydrocarbylhaloaluminoxane composition; or

B) in the absence of an organic or inorganic catalyst support or carrier to form a liquid reaction mixture, and bringing a catalyst support or carrier into contact with said reaction mixture during or after completion of said partial hydrolysis but before any substantial crystal formation takes place in said reaction mixture, to form the supported hydrocarbylhaloaluminoxane composition.

21. A method of claim 20 wherein said support or carrier is an inorganic catalyst support.

22. A method of claim 21 wherein said inorganic support or carrier used is comprised of a zeolite, magnesium chloride, or at least one inorganic oxide.

23. A method of claim 21 wherein said inorganic support or carrier used is silica, alumina, or silica-alumina.

24. A method of claim 21 wherein the catalyst support or carrier used is silica.

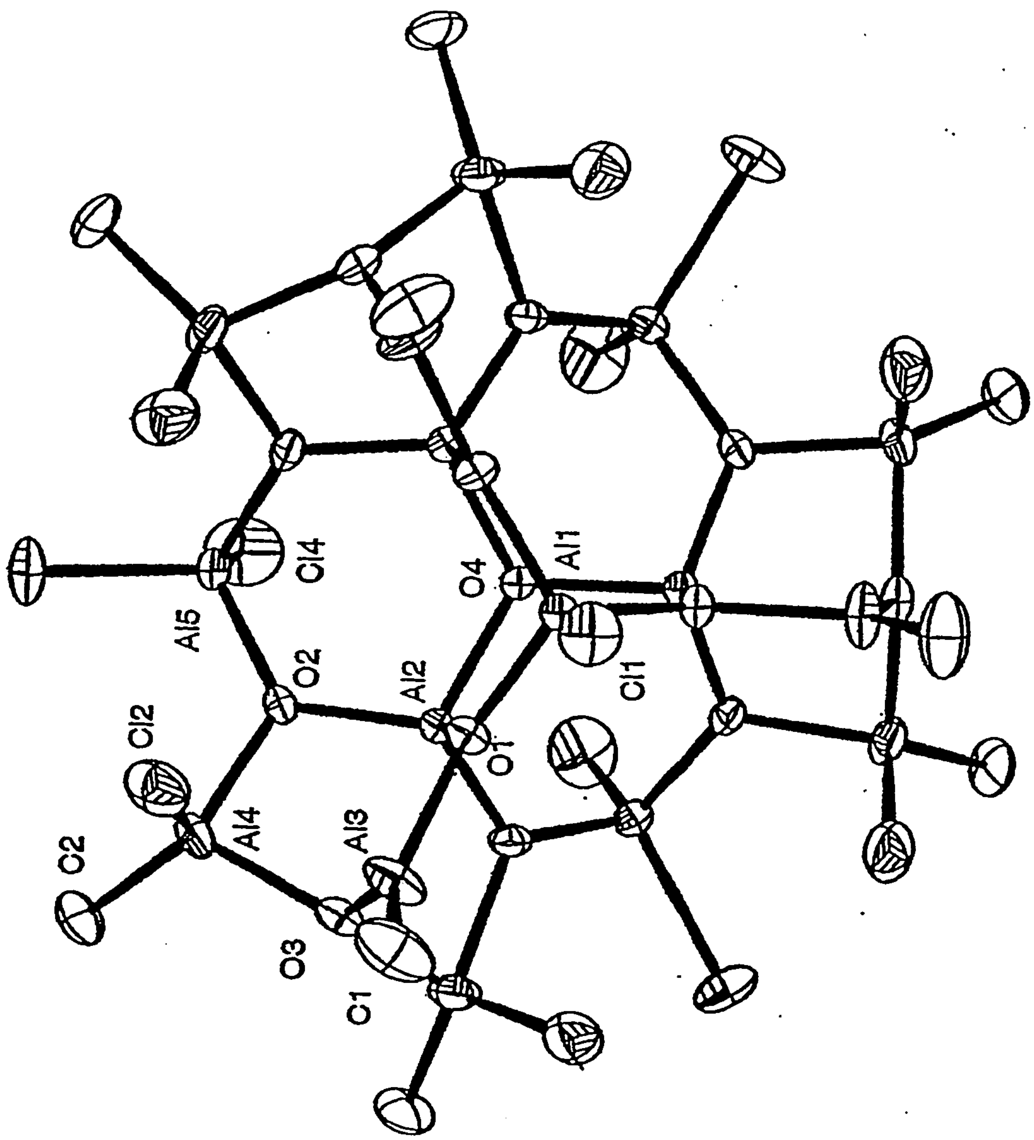
25. A catalyst composition formed from interaction between:

A) components comprising (i) a compound of any of claims 1-10 and (ii) an inorganic or organic metal catalyst compound in the presence or absence of a catalyst support or carrier, or

B) components comprising (i) a composition of any of claims 11-15 and (ii) an inorganic or organic metal catalyst compound.

26. A method of forming a catalyst composition of Claim 25 which method comprises causing components (i) and (ii) of A) or the components (i) and (ii) of B) to interact to form a catalyst composition.

Chloro-Methylaluminoxane
(C-MAO)



$Me_9Al_{16}O_{13}Cl_{13}$

Figure 1

PCT/US 03/09123

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J31/14 C07F5/06 C08F4/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SIERGIEJCZYK, LESZEK ET AL: "Reactions of methylaluminum halides with lead oxide" POLIMERY, vol. 31, no. 10, 1986, pages 397-8, XP009013039 ISSN: 0032-2725 the whole document	1,2, 11-15, 20-26
A	WO 00 22007 A (DU PONT) 20 April 2000 (2000-04-20) cited in the application claim 1; examples	1-26
A	EP 0 919 557 A (MERCK PATENT GMBH) 2 June 1999 (1999-06-02) the whole document	1-26

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 July 2003	14/07/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Elliott, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 03617 A (EXXON CHEMICAL PATENTS INC) 29 January 1998 (1998-01-29) page 10, line 29 - line 37 -----	1-26

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 0022007	A	20-04-2000	AU	1201700	A	01-05-2000
			BR	9914778	A	03-07-2001
			CA	2341526	A1	20-04-2000
			CN	1323322	T	21-11-2001
			EP	1137676	A1	04-10-2001
			JP	2002527543	T	27-08-2002
			WO	0022007	A1	20-04-2000
			US	6306986	B1	23-10-2001
EP 0919557	A	02-06-1999	DE	19753135	A1	02-06-1999
			EP	0919557	A1	02-06-1999
			JP	11269180	A	05-10-1999
WO 9803617	A	29-01-1998	AU	722983	B2	17-08-2000
			AU	3660197	A	10-02-1998
			EP	0914409	A1	12-05-1999
			JP	2000514864	T	07-11-2000
			WO	9803617	A1	29-01-1998
			US	6066603	A	23-05-2000